



# Adsorptive denitrogenation of model fuels with porous metal-organic frameworks (MOFs): Effect of acidity and basicity of MOFs

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## ABSTRACT

To understand the effect of the acidity or basicity of porous metal-organic frameworks (MOFs) on the adsorptive removal of nitrogen-containing compounds (NCCs), an MOF (MIL-100(Cr)) was modified to impart acidity or basicity onto the MOFs. The modification was done by grafting ethylenediamine and aminomethanesulfonic acid onto coordinatively unsaturated sites of the MOF, MIL-100(Cr). The adsorptive removal of a basic quinoline or benzothiophene can be improved noticeably, especially at low concentrations, with the introduction of an acidic site; however, a basic MOF causes a severe decrease in the adsorptive performance for a basic adsorbate such as quinoline. The effect of the interaction of the base–base on adsorption was more severe or detrimental for a hard base quinoline than for a soft base benzothiophene. Functionalized MOFs show a slightly decreased adsorption for a neutral adsorbate such as indole probably because of the decreased porosity of the MOFs compared with the virgin MOF without functionalization. Moreover, a functionalized MOF (with  $-\text{SO}_3\text{H}$  group) can be used several times after simple washing with acetone. From the present research, it may be concluded that acid–base interactions between NCCs and MOFs will lead to favorable adsorptive removal of NCCs. However, for the adsorptive removal of a neutral adsorbate such as indole, another adsorption mechanism (such as  $\pi$ -complexation or hydrogen-bonding) is needed for high uptake and efficient removal.

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## 1. Introduction

With an increasing population worldwide, energy and the environment have been two major concerns of humans this century. Because of limited fossil fuels and a large demand for energy, fossil fuels with many contaminants (S, N, metals) and high viscosity will be utilized in the next several decades [1–4]. Therefore, various efforts have been devoted to remove sulfur-containing compounds (SCCs) or nitrogen-containing compounds (NCCs) from fuels because of a bad effect of SCCs and NCCs on the environment and on the catalyst life.

Especially, NCCs [5,6] are one of the contaminants that should be removed since NCCs have a bad effect on both catalysts and conventional hydrodesulfurization (HDS) processes. NCCs have been usually removed by hydrodenitrogenation (HDN) in the presence of expensive hydrogen at high temperature and pressure [5–7]; therefore, HDN is an energy-intensive and costly process. Moreover, HDN, compared with HDS, is an inefficient process because the nitrogen in NCCs can be removed only after hydrogenation of the hetero-rings. Therefore, much hydrogen is consumed in the HDN

process, and HDN, compared with HDS, is a kinetically slow process [5,6,8].

Adsorptive-denitrogenation (ADN) is one of the choices that can be used to remove NCCs from fuels because ADN does not require expensive hydrogen, high temperature and high pressure [5–7]. So far, several adsorbents such as activated carbon [5,6,9–13], Cu(I)-Y zeolites [7,14], HCl-loaded silica-aluminas [15], ion exchange resins [16], meso-silicas [17,18], Ti-HMSs [19], microporous carbons [20], activated aluminas [12], Ni-based adsorbents [12], and NiMOs [21] have been used for ADN.

Recently, the number of materials exhibiting permanent nanoporosity has rapidly expanded due in large part to the introduction of porous materials including metal-organic frameworks (MOFs) or coordination polymers [22–24]. The porous MOFs have attracted considerable attention due to an easily tunable crystalline hybrid network with a high and regular porosity. Moreover, MOFs have lots of potential applications including gas adsorption/storage, separation, catalysis, adsorption of organic molecules, drug delivery, luminescence, electrode materials, carriers for nanomaterials, magnetism, polymerization, imaging, and so on [22–27]. The MOFs have also been studied in the field of adsorptive removal of hazardous materials [28–30] including adsorptive desulfurization (ADS) [31–35] and adsorptive denitrogenation (ADN) [36,37] processes. Maes et al. [36] showed that MOFs, selected and reduced

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suitably, could be used in an ADN and/or ADS process. Moreover, the adsorption could be explained with the concept of HSAB (hard and soft acid and base). MIL-101(Cr) had a remarkable adsorption capacity for NCCs and was effective in removing various NCCs [37]. However, so far, there is little effort to understand the interactions between NCCs and MOFs even though the interactions will be very important to understand the ADN process and physico-chemical properties of the MOFs. Moreover, understanding the interactions will lead to the potential application of MOFs in drug storage/delivery [38,39] and removal of harmful materials [28–30].

In this work, an ADN process has been studied with MOFs especially after modification to impart an acidity and basicity since these properties (including type of Lewis or Brønsted acid/base) may have influence on the adsorptive removal. MOFs such as Cu-BTC (Cu-benzenetricarboxylate) [40], MIL-100(Cr) (Cr-benzenetricarboxylate) [41] and MIL-101(Cr) (Cr-benzenedicarboxylate) [42] have been used for the adsorption of quinoline (QUI), indole (IND) and benzothiophene (BT) as a basic (hard) NCC, a neutral NCC and a basic (soft) SCC, respectively. MIL-100(Cr) has been studied in more detail after imparting an acidity or basicity. Through this study, an understanding of the interaction between MOFs and NCCs was elucidated. Additionally, a facile modification method of the MOFs was suggested to impart a high/selective adsorption capacity/site for ADN.

## 2. Experimental

### 2.1. Chemicals and synthesis of adsorbents

All of the chemicals such as benzothiophene (BT), quinoline (QUI) and indole (IND) utilized in this study were commercial products and used without further purification. The MOFs (Cu-BTC, MIL-100(Cr), and MIL-101(Cr)) used in this study were synthesized as previously described [43–45]. The syntheses were carried out hydrothermally or solvothermally under microwave (Mars-5, CEM, maximum power of 1200 W) irradiation to take advantage of fast synthesis [46,47] or electric heating. Detailed information on the chemicals and MOFs syntheses are shown in the supporting information.

MIL-100(Cr) was functionalized as previously described [48,49]. Ethylenediamine (ED) and aminomethanesulfonic acid (AMSA) were used as sources of  $\text{—NH}_2$  and  $\text{—SO}_3\text{H}$  groups, respectively, and the common  $\text{—NH}_2$  functional group was coordinated on open metal sites or coordinatively unsaturated sites (CUSs) of the MOF MIL-100(Cr). Before functionalization, MIL-100(Cr) was dehydrated at  $150^\circ\text{C}$  for 12 h in a vacuum oven to generate CUSs. Dehydrated MIL-100(Cr) (0.5 g) was suspended in 30 ml anhydrous toluene. To this suspension, 1 mmol of ethylenediamine was added and the mixture was refluxed for 12 h with a continuous stirring. The product was filtered and washed with ethanol/de-ionized water, and then dried at room temperature. The product was denoted as ED-MIL-100(Cr).  $\text{SO}_3\text{H}$ -grafted MIL-100(Cr) was similarly obtained. In a typical procedure, 0.5 g dehydrated MIL-100(Cr) was suspended in 30 ml absolute ethanol and 1 mmol AMSA was added. The mixture was refluxed for 12 h with continuous stirring. The product was filtered and washed with deionized water, and then dried at room temperature. The product was denoted as AMSA-MIL-100(Cr).

### 2.2. Characterization

The X-ray powder diffraction patterns were obtained with a diffractometer D2 Phaser (Bruker, with  $\text{CuK}\alpha$  radiation). FT-IR spectra were recorded on a Jasco FTIR-4100 equipped with an ATR accessory. Elemental analyses of the adsorbates were done using an

elemental analyzer (Thermo Fisher, Flash-2000) with a TCD detector. The nitrogen adsorptions and desorptions of the adsorbents were obtained at  $-196^\circ\text{C}$  with a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation at  $150^\circ\text{C}$  for 12 h.

### 2.3. General procedures for the adsorption experiments

Stock solutions (10,000 ppm each) for a model fuel were prepared separately for the three adsorbates (BT, QUI and IND) by dissolving them in a mixture of 75 vol% *n*-octane and 25 vol% *p*-xylene. Combined solutions of different concentrations were prepared by successive dilution and mixing of the three solutions. A solution with a fixed concentration of NCCs and SCCs (400 ppm BT, 200 ppm QUI and 200 ppm IND) was used to determine the relative adsorption capacity with various adsorption times. Solutions having various concentrations of BT (300–2400 ppm), QUI (150–1200 ppm) and IND (150–1200 ppm) were used to obtain adsorption isotherms after adsorption for 2 h.

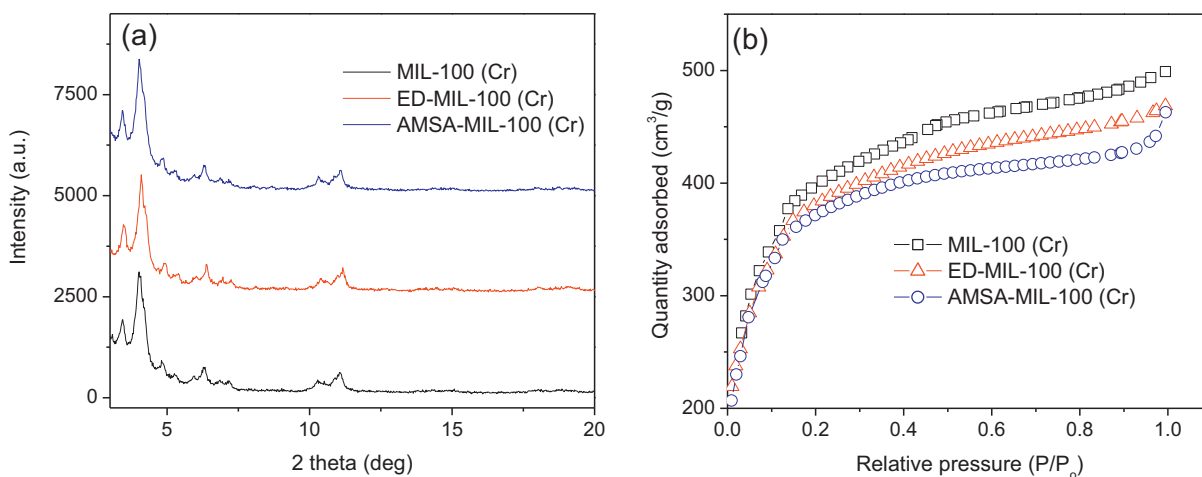
Before adsorption, the adsorbents were dried in a vacuum oven at  $150^\circ\text{C}$  for 12 h and kept in a desiccator. For every adsorption experiment, 10 ml of solution and 10 mg of adsorbent were mixed and stirred magnetically for a predetermined time (2–120 min). The adsorption temperature was maintained at  $25^\circ\text{C}$ . After adsorption, the solution was separated from the solid with a syringe filter and analyzed with a GC (DS Science, IGC 7200) equipped with an FID. The maximum adsorption capacity ( $Q_0$ ) was calculated with the Langmuir adsorption isotherms. More details on the adsorption isotherms and maximum adsorption capacities are described in the supporting information.

After the first run of adsorption with the fresh MOFs, the used MOFs were regenerated by washing with several organic solvents. For this, filtered MOFs were immersed in a solvent and kept in a sonification bath for 1 h. After that, the MOFs were filtered and the operation was continued for one more time. Then the adsorbent was dried in a vacuum oven and the adsorption operations were carried out as previously described method. Adsorptions with regenerated MOFs were repeated up to the fourth run.

## 3. Results and discussion

### 3.1. Textural properties and characterization of the adsorbents

The synthesized MOFs had the crystalline structures of Cu-BTC, MIL-100(Cr) and MIL-101(Cr) and did not contain impurities as confirmed by the XRD patterns (supporting information, Fig. S1). The virgin and modified MIL-100(Cr)s had the typical XRD patterns of the MIL-100(Cr) structure and the nitrogen adsorption results show that the materials had high porosities useful for adsorptions (Fig. 1). Even though the XRD patterns of MIL-100(Cr) did not change with modification, the porosity decreased slightly with the modification (porosity was on the order of  $\text{MIL-100(Cr)} > \text{ED-MIL-100(Cr)} > \text{AMSA-MIL-100(Cr)}$ ) as shown in Table 1 and Fig. 1) probably because of the extra volumes of the organic moieties used for modification. The ED-MIL-100(Cr) and AMSA-MIL-100(Cr) contained N (3.72 wt% of the MOF) and S (1.12 wt% of the MOF), respectively (based on chemical analysis), because of the functionalization with ethylenediamine (ED) and aminomethanesulfonic acid (AMSA). The successful grafting of the MIL-100(Cr) with ED and AMSA could be confirmed with FTIR spectra (supporting information, Fig. S2). For the ED-MIL-100(Cr), C–N bond stretching and N–H plane stretching [51] were observed at  $1033\text{ cm}^{-1}$  and  $1594\text{ cm}^{-1}$ , respectively. In the case of AMSA-MIL-100(Cr), the bands at  $1074\text{ cm}^{-1}$  and  $1034\text{ cm}^{-1}$  could be assigned to the asymmetric S–O stretching vibrations [52,53].

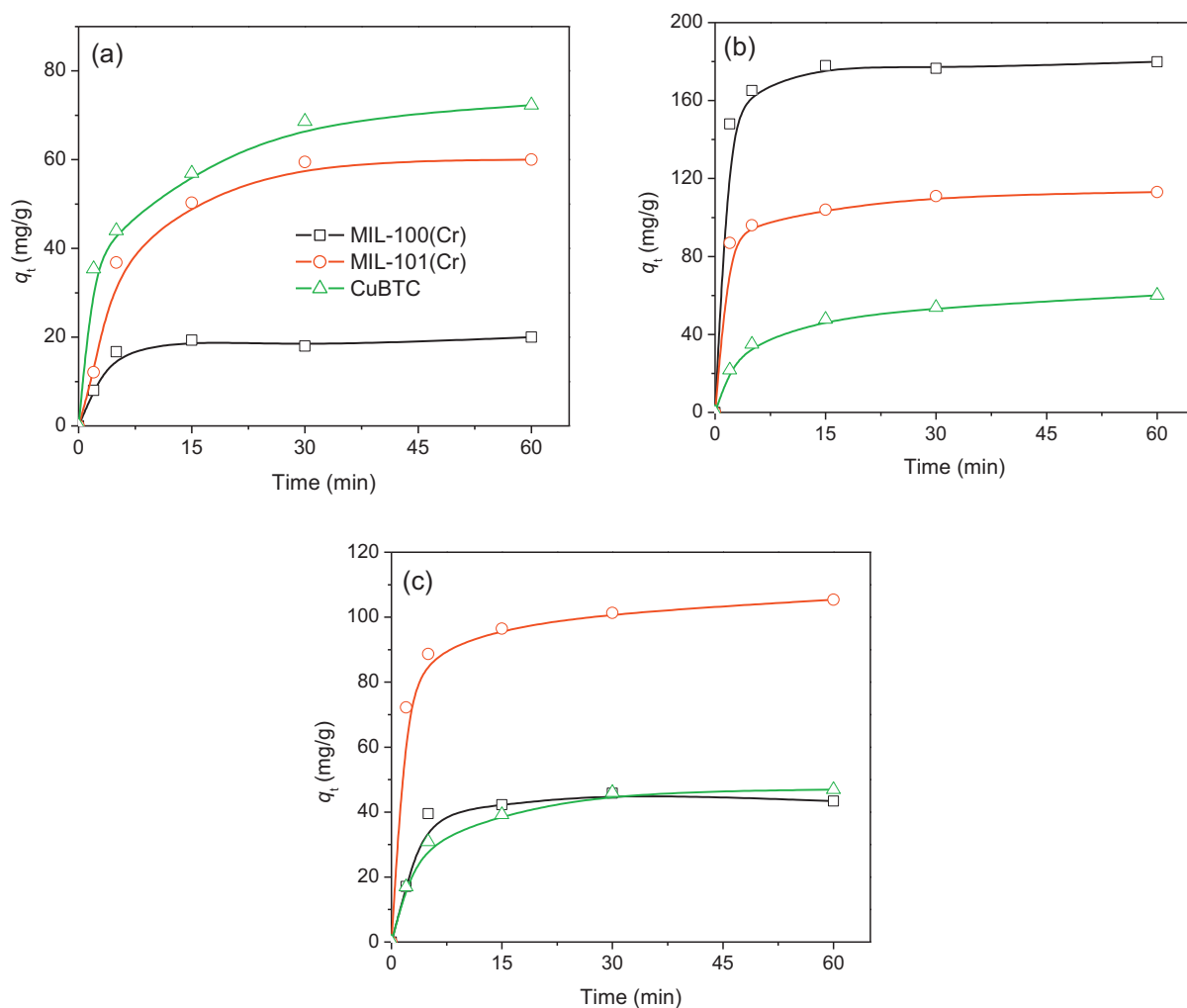


**Fig. 1.** (a) XRD patterns and (b) nitrogen adsorption isotherms of virgin and grafted MIL-100(Cr)s.

### 3.2. Adsorptive removal with virgin adsorbents

The three virgin MOFs were used in the adsorption of NCCs and SCCs in order to estimate the applicability of the materials in the ADN and ADS. As shown in Fig. 2, the Cu-BTC was the

most effective in the adsorption of BT, which agrees with the results of Maes et al. [36]. Since SCCs are soft bases, BT may be effectively adsorbed over a soft Lewis acid Cu<sup>2+</sup> of Cu-BTC. The performance of the MOFs for the adsorptive removal of QUI was on the order of MIL-100(Cr) > MIL-101(Cr) > Cu-BTC. IND was adsorbed



**Fig. 2.** Effect of contact time on the adsorption of (a) BT; (b) QUI and (c) IND over the three MOFs. The hydrocarbon solutions initially contain 400 ppm BT, 200 ppm QUI and 200 ppm IND.

**Table 1**Physiochemical properties and the maximum adsorption capacities ( $Q_0$ ) of virgin and grafted MIL-100(Cr)s.

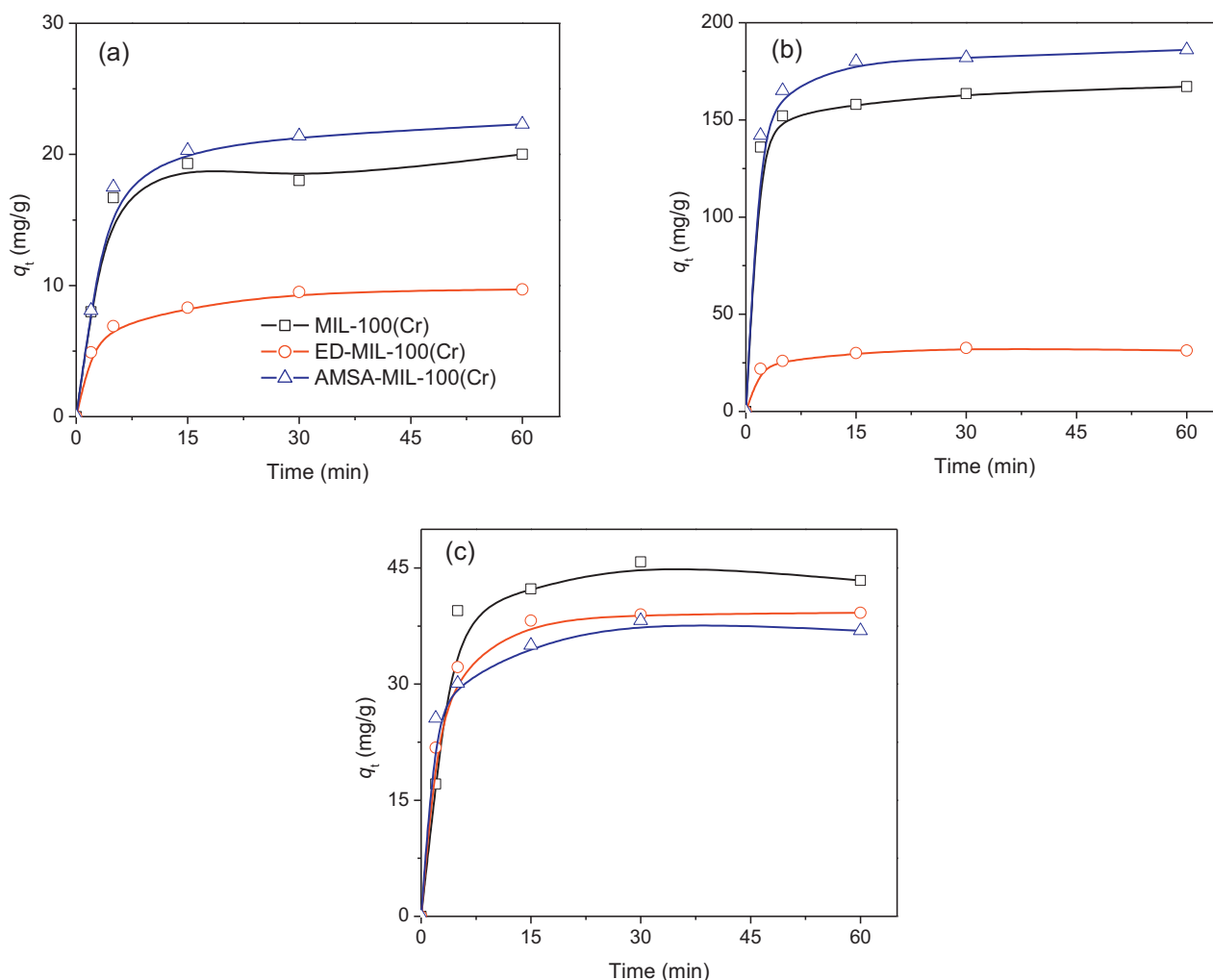
Adsorbent	BET surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )	Adsorbate	$Q_0$ (mg/g)	$Q_0$ ( $\text{cm}^3/\text{g}$ )	Total $Q_0$ ( $\text{cm}^3/\text{g}$ )
MIL-100(Cr)	1462	0.77	BT	28	0.03	0.42
			QUI	342	0.32	
			IND	103	0.08	
ED-MIL-100(Cr)	1395	0.73	BT	23	0.02	0.20
			QUI	119	0.11	
			IND	94	0.08	
AMSA-MIL-100(Cr)	1351	0.72	BT	31	0.03	0.41
			QUI	323	0.29	
			IND	97	0.08	

most effectively over MIL-101(Cr), which agrees with a previous report [36].

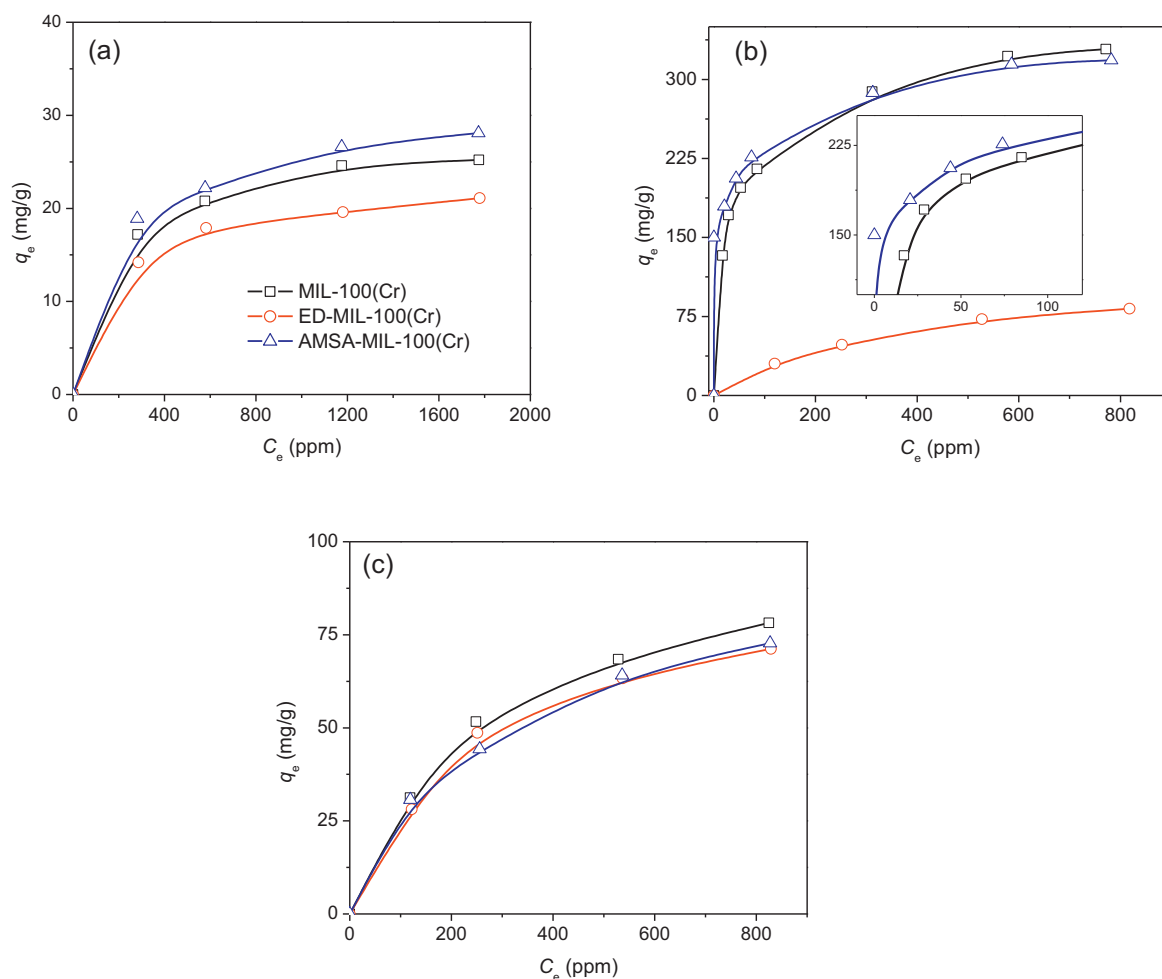
### 3.3. Effect of functionalization of MIL-100(Cr)

Since coal-derived fuels, which will be very important in the future, contain mainly basic NCCs such as QUI [50] and basic NCCs inhibit catalysis severely [19] or adsorb [6] strongly onto catalytic sites, MIL-100(Cr) was selected as the MOF for further research on ADN. The MIL-100(Cr)s, after being functionalized to impart an acidic or basic site, were used in ADN and ADS, and the results are shown in Fig. 3. Sulfated MIL-100(Cr) (AMSA-MIL-100(Cr)) was

quite effective in the adsorptive removal of QUI and BT probably because of the basicity of the adsorbates. However, the basic MIL-100(Cr) (ED-MIL-100(Cr)) had shown poor performance in the adsorption of QUI and BT. Interestingly, any functionalized MIL-100(Cr) such as ED-MIL-100(Cr) and AMSA-MIL-100(Cr) had decreased performance in the adsorption of IND probably because of the neutral IND and decreased porosity of the functionalized MOFs. In any case, the adsorption rates were very high showing virtually complete adsorption in 15 min (Fig. 3), which suggests the efficiency of MIL-100(Cr)s in the ADN and ADS. This might be due to the sufficiently large pore size of the MIL-100(Cr)s even after the modifications.



**Fig. 3.** Effect of contact time on the adsorption of (a) BT; (b) QUI and (c) IND over virgin and grafted MIL-100(Cr)s. The hydrocarbon solutions initially contain 400 ppm BT, 200 ppm QUI and 200 ppm IND.



**Fig. 4.** Adsorption isotherms for (a) BT; (b) QUI and (c) IND over virgin and grafted MIL-100(Cr)s. The inset of (b) shows the enlarged adsorption isotherms at low QUI equilibrium concentrations.

### 3.4. The adsorption isotherms and separation factor

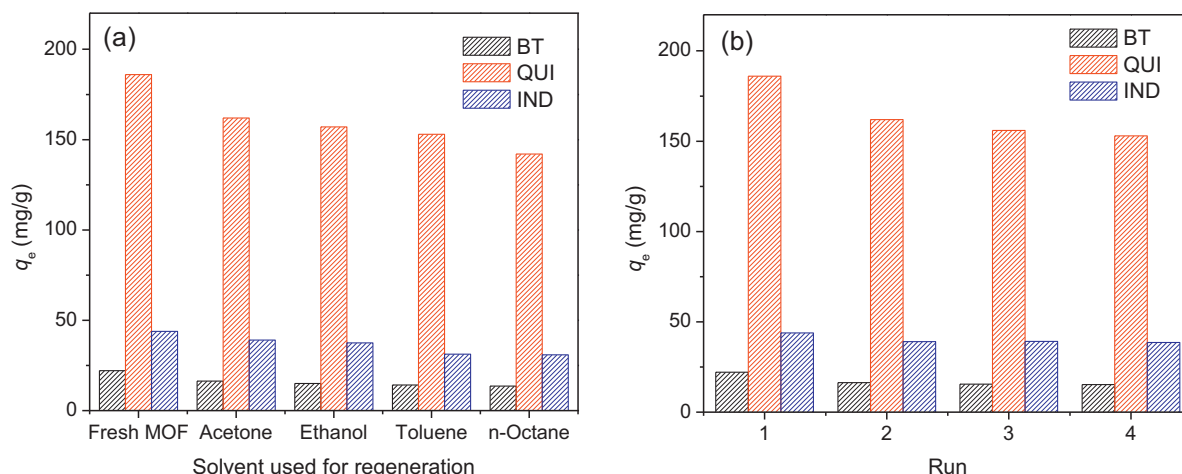
To understand further the ADN and ADS over the modified MIL-100(Cr)s, adsorption isotherms were obtained. As shown in Fig. 4, the general adsorptive performances did not change for the overall concentrations. In other words, the AMSA-MIL-100(Cr) is very effective in removing basic materials such as BT and QUI (Fig. 4a and the inset of Fig. 4b). Three different equations, i.e. Langmuir, Freundlich and Temkin isotherms were used to interpret the adsorption result as shown in supporting Figs. 3–5. Correlation factors ( $R^2$  values) of the three isotherms (supporting Table S1) suggest that, Langmuir equation is the best choice to interpret adsorption result. Moreover, Langmuir adsorption might be the best option in this study because of monolayer adsorption through chemisorptions or adsorptions in microporous materials. Therefore, the adsorption capacities shown in Table 1 for BT, QUI and IND were calculated using the Langmuir plots (supporting Fig. S3). Based on the total  $Q_0$  (Table 1, in  $\text{cm}^3/\text{g}$ ) of the three adsorbates, it can be understood that only 32–57% of the total pore volume of the MOFs is occupied with BT, QUI and IND, suggesting the possible adsorption of aromatic compound (*p*-xylene in this study) over the MOFs even though the preference of adsorption for aromatics is lower than that of the NCCs or SCCs [7]. This may suggest the adsorption of NCCs or SCCs can be improved further if a more suitable adsorption site can be introduced into the MOFs.

Even though the adsorption capacity for QUI at saturation (Table 1 and Fig. 4b) was decreased a bit with the functionalized

AMSA, the adsorption for QUI was very effective at low concentration (see the inset of Fig. 4b). The low adsorption capacity of AMSA-MIL-100(Cr) at saturation might be due to the decreased porosity, and the effective adsorption at low concentration was due to favorable interactions between an acid (AMSA-MIL-100(Cr)) and a base (QUI), which has been observed in ADN with activated carbons [5]. In commercial ADN, the adsorption at low concentration should be very important because of the low concentration of NCCs in commercial fuels; therefore, AMSA-MIL-100(Cr) might be effective in the ADN of commercial fuels. However, the basic ED-MIL-100(Cr) is very poor in the adsorptive removal of a basic QUI and also had a poor performance in adsorption of a soft base, BT. The adsorptive performances of the modified MIL-100(Cr)s (ED-MIL-100(Cr) and AMSA-MIL-100(Cr)) for IND was decreased with the functionalization because of the decreased porosity (due to the grafted ED and AMSA). For adsorptive removal of neutral NCCs, another adsorption mechanism such as  $\pi$ -complexation [7] and hydrogen-bonding [5,16] may be needed.

The adsorption may be understood further with a dimensionless constant called the separation factor or equilibrium parameter,  $R_L$  [54]. Supporting Fig. S6 shows the calculated  $R_L$  values versus the initial concentrations of the three adsorbates with MIL-100(Cr)s. All the  $R_L$  values were from 0 to 1, indicating the favorable adsorption of QUI, IND and BT over the three adsorbents [55] at the conditions being studied. Additionally, it can be understood that the adsorption was most favorable for QUI over AMSA-MIL-100(Cr) among the three adsorbents for the three adsorbates at similar initial





**Fig. 5.** (a) Effect of solvents applied in the regeneration of the used AMSA-MIL-100(Cr) on the adsorptive removal of BT, QUI and IND; (b) effect of regeneration cycles on the performances of adsorptive removal of BT, QUI and IND over regenerated AMSA-MIL-100(Cr) by washing with acetone. The adsorption was done for 2 h using hydrocarbon solutions containing 400 ppm BT, 200 ppm QUI and 200 ppm IND.

concentration since the separation factor  $R_L$  [56,57] was the lowest in the case of the QUI adsorption over AMSA-MIL-100(Cr). This is in accordance with the adsorption results shown in Figs. 3 and 4 (especially, the inset in Fig. 4b).

Based on the above results, it may be concluded that the adsorption of QUI and BT can be improved considerably with the incorporation of an acid site in MIL-100(Cr). The beneficial effect of an acidic site on the adsorption of basic NCCs is in accordance with the result obtained with activated carbons [5]. On the contrary, a basic moiety (grafted ED) on the MOF caused a negative effect on the adsorption of QUI and BT. Moreover, the adsorptive performances of functionalized MIL-100(Cr) for neutral IND were negatively affected by both the acidic and basic functional groups. All of the obtained results may be explained by (1) the favorable interaction between an acid (AMSA-MIL-100(Cr)) and a base (QUI or BT); (2) the unfavorable interaction between a base (ED-MIL-100(Cr)) and a base (QUI or BT); and (3) the negligible interaction between an acid (AMSA-MIL-100(Cr)) or a base (ED-MIL-100(Cr)) and a neutral adsorbate (IND).

### 3.5. Reusability

Commercial applications of an adsorptive removal may rely on the reusability of an adsorbent. In this study the reusability of the AMSA-MIL-100(Cr) was estimated after solvent washing of the used MOFs. Several solvents were applied to re-activate the pre-adsorbed MOFs since solvents with various polarities (such as toluene [6,36], methylisobutyl ketone [17], ethanol [19], and acetone [37]) have been applied so far. As shown in Fig. 5, the performance of the used AMSA-MIL-100(Cr) after solvent washing depended on the applied solvent; and the reusability of AMSA-MIL-100(Cr) for QUI decreased on the order of acetone > ethanol > toluene > n-octane washing (Fig. 5a). The intact structure of the regenerated AMSA-MIL-100(Cr) could be confirmed with the XRD (data not shown) and FTIR (supporting information, Fig. S7). The performances of the regenerated AMSA-MIL-100(Cr), after washing with acetone, was a bit low compared to the fresh AMSA-MIL-100(Cr); however, the adsorbed amounts for QUI, BT and IND changed little after the second run (Fig. 5b), suggesting the application of the AMSA-MIL-100(Cr) for commercial fuels. Additionally, this stable performance and intact structure may be agreeable with the stability of the grafted functional groups on MOFs in adsorption [29] and hydrogenation [48] in water solvent.

## 4. Conclusion

Based on the adsorption study, a few important conclusions can be drawn. For adsorptive removal of a hard base, an acidic MOF will be helpful because of the favorable interaction between an acid (MOF) and a base (adsorbate). Moreover, an acid–base interaction may be helpful to adsorb a basic adsorbate especially at low concentration, which is important in commercial applications. An acid–base interaction will be also favorable for the adsorptive removal of a soft base such as sulfur-containing compounds. However, functionalization to load an acid or base site is not helpful in improving the adsorptive performances for a neutral adsorbate such as indole because of the negligible interaction between neutral NCCs and acidic or basic adsorbents. The acid-functionalized MOF (AMSA-MIL-100(Cr)) may be reused several times by simply washing the pre-adsorbed MOF with acetone. Based on the favorable and rapid uptake of a basic NCC over a functionalized MOF and the reusability of the MOF, it is suggested that MOFs, suitably modified, may be used in ADN especially for basic NCCs.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.09.020>.

## References

- [1] V.C. Srivastava, RSC Advances 2 (2012) 759–783.
- [2] B. Pawelec, R.M. Navarro, J.M. Campos-Martin, J.L.G. Fierro, Catalysis Science and Technology 1 (2011) 23–42.
- [3] A. Stanislaus, A. Marafi, M.S. Rana, Catalysis Today 153 (2010) 1–68.
- [4] A. Samokhvalov, B.J. Tatarchuk, Catalysis Reviews: Science and Engineering 52 (2010) 381–410.
- [5] M. Almarri, X. Ma, C. Song, Energy and Fuels 23 (2009) 3940–3947.
- [6] M. Almarri, X. Ma, C. Song, Industrial and Engineering Chemistry Research 48 (2009) 951–960.

- [7] J. Hernandez-Maldonado, R.T. Yang, *Angewandte Chemie International Edition* 43 (2004) 1004–1006.
- [8] S. Eijssbouts, V.H.J. De Beer, R. Prins, *Journal of Catalysis* 127 (1991) 619–630.
- [9] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, *Energy and Fuels* 18 (2004) 644–651.
- [10] N. Li, M. Almarri, X.-L. Ma, Q.-F. Zha, *New Carbon Materials* 26 (2011) 470–478.
- [11] J. Wen, X. Han, H. Lin, Y. Zheng, W. Chu, *Chemical Engineering Journal* 164 (2010) 29–36.
- [12] J.H. Kim, X. Ma, A. Zhou, C. Song, *Catalysis Today* 111 (2006) 74–83.
- [13] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, *Applied Catalysis B* 49 (2004) 219–225.
- [14] D. Liu, J. Gui, Z. Sun, *Journal of Molecular Catalysis A: Chemical* 291 (2008) 17–21.
- [15] C.A. Audeh, *Industrial and Engineering Chemistry Product Research and Development* 22 (1983) 276–279.
- [16] L.-L. Xie, A. Favre-Reguillon, X.-X. Wang, X. Fu, M. Lemaire, *Journal of Chemical and Engineering Data* 55 (2010) 4849–4853.
- [17] A. Koriakin, K.M. Ponvel, C.-H. Lee, *Chemical Engineering Journal* 162 (2010) 649–655.
- [18] J.-M. Kwon, J.-H. Moon, Y.-S. Bae, D.-G. Lee, H.-C. Sohn, C.-H. Lee, *ChemSusChem* 1 (2008) 307–309.
- [19] H. Zhang, G. Li, Y. Jia, H. Liu, *Journal of Chemical and Engineering Data* 55 (2010) 173–177.
- [20] B. Sun, G. Li, X. Wang, *Journal of Natural Gas Chemistry* 19 (2010) 471–476.
- [21] M. Sun, A.E. Nelson, J. Adjaye, *Catalysis Today* 109 (2005) 49–53.
- [22] G. Férey, *Chemical Society Reviews* 37 (2008) 191–214.
- [23] S. Kitagawa, R. Kitaura, S.-I. Noro, *Angewandte Chemie International Edition* 43 (2004) 2334–2375.
- [24] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, *Nature* 423 (2003) 705–714.
- [25] H. Wu, Q. Gong, D.H. Olson, J. Li, *Chemical Reviews* 112 (2012) 836–868.
- [26] J.-R. Li, J. Sculley, H.-C. Zhou, *Chemical Reviews* 112 (2012) 869–932.
- [27] N. Stock, S. Biswas, *Chemical Reviews* 112 (2012) 933–969.
- [28] Z. Hasan, J. Jeon, S.H. Jhung, *Journal of Hazardous Materials* 209–210 (2012) 151–157.
- [29] E. Haque, J.E. Lee, I.T. Jang, Y.K. Hwang, J.-S. Chang, J. Jegal, S.H. Jhung, *Journal of Hazardous Materials* 181 (2010) 535–542.
- [30] E. Haque, J. Jun, S.H. Jhung, *Journal of Hazardous Materials* 185 (2011) 507–511.
- [31] K.A. Cychosz, A.G. Wong-Foy, A.J. Matzger, *Journal of the American Chemical Society* 131 (2009) 14538–14543.
- [32] N.A. Khan, S.H. Jhung, *Angewandte Chemie International Edition* 51 (2012) 1198–1201.
- [33] N.A. Khan, J.W. Jun, J.H. Jeong, S.H. Jhung, *Chemical Communications* 47 (2011) 1306–1308.
- [34] N.A. Khan, S.H. Jhung, *Fuel Processing Technology* 100 (2012) 49–54.
- [35] S. Achmann, G. Hagen, M. Hämmerle, I. Malkowsky, C. Kiener, R. Moos, *Chemical Engineering and Technology* 33 (2010) 275–280.
- [36] M. Maes, M. Trekels, M. Boulhout, S. Schouteden, F. Vermoortele, L. Alaerts, D. Heurtaux, Y.-K. Seo, Y.K. Hwang, J.-S. Chang, I. Beurroies, R. Denoyel, K. Temst, A. Vantomme, P. Horcajada, C. Serre, D.E. De Vos, *Angewandte Chemie International Edition* 50 (2011) 4210–4214.
- [37] A.L. Nuzhdin, K.A. Kovalenko, D.N. Dybtsev, G.A. Bukhtiyarova, *Mendeleev Communications* 20 (2010) 57–58.
- [38] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J.F. Eubank, E. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y.K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, R. Gref, *Nature Materials* 9 (2010) 172–178.
- [39] P. Horcajada, C. Serre, G. Maurin, N.A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, *Journal of the American Chemical Society* 130 (2008) 6774–6780.
- [40] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, *Science* 283 (1999) 1148–1150.
- [41] G. Férey, C. Serre, C.M. Draznieks, F. Millange, S. Surble, J. Dutour, I. Margiolaki, *Angewandte Chemie International Edition* 43 (2004) 6296–6301.
- [42] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I. Margiolaki, *Science* 309 (2005) 2040–2042.
- [43] N.A. Khan, E. Haque, S.H. Jhung, *Physical Chemistry Chemical Physics* 12 (2010) 2625–2631.
- [44] T.K. Trung, N.A. Ramsahye, P. Trens, N. Tanchoux, C. Serre, F. Fajula, G. Férey, *Microporous and Mesoporous Materials* 134 (2010) 134–140.
- [45] N.A. Khan, S.H. Jhung, *Crystal Growth and Design* 10 (2010) 1860–1865.
- [46] S.H. Jhung, J.-H. Lee, J.W. Yoon, C. Serre, G. Férey, J.-S. Chang, *Advanced Materials* 19 (2007) 121–124.
- [47] E. Haque, N.A. Khan, J.H. Park, S.H. Jhung, *Chemistry – A European Journal* 16 (2010) 1046–1052.
- [48] Y.K. Hwang, D.-Y. Hong, J.-S. Chang, S.H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angewandte Chemie International Edition* 47 (2008) 4144–4148.
- [49] D.-Y. Hong, Y.K. Hwang, C. Serre, G. Férey, J.-S. Chang, *Advanced Functional Materials* 19 (2009) 1537–1552.
- [50] N. Li, X. Ma, Q. Zha, C. Song, *Energy and Fuels* 24 (2010) 5539–5547.
- [51] K.-J. Huang, D.-J. Niu, J.-Y. Sun, C.-H. Han, Z.-W. Wu, Y.-L. Li, X.-Q. Xiong, *Colloids and Surfaces B: Biointerfaces* 82 (2011) 543–549.
- [52] L.K. Noda, R.M. de Almeida, L.F.D. Probst, N.S. Gonçalves, *Journal of Molecular Catalysis A: Chemical* 225 (2005) 39–46.
- [53] M.K. Mishra, B. Tyagi, R.V. Jasra, *Industrial and Engineering Chemistry Research* 42 (2003) 5727–5736.
- [54] T.W. Weber, R.K. Chakravorti, *AIChE Journal* 20 (1974) 228–238.
- [55] Y. Önal, C. Akmil-Basar, C. Sarıcı-Özdemir, *Journal of Hazardous Materials* 148 (2007) 727–734.
- [56] Y.-S. Ho, T.-H. Chiang, Y.-M. Hsueh, *Process Biochemistry* 40 (2005) 119–124.
- [57] H. Liu, Y. Dong, H. Wang, Y. Liu, *Journal of Environmental Sciences* 22 (2010) 1513–1518.